Reduction of harmful gases in gas mixtures from
pyrotechnic reactions

Background of the Invention

The present invention relates to the reduction of
harmful gases in gas mixtures from pyrotechnic
reactions.

5   An airbag system has, as basic components, impact sack,
gas generator and trigger device which initiates an
electric ignition in the gas generator as required, when
a previously specified triggering threshold is exceeded.
As a result, a gas is generated within a very short time
10   (approx. 40 ms, depending on the airbag module), and
flows into an air sack which spreads out between the
passengers in the vehicle and the site of impact. The
gas-producing substance (expanding agent, propellant)
used is a solid mixture of fuel, oxidizing agent and
15   additives in the form of tablets, which reacts within
the combustion chamber in about 10 to 40 ms after
ignition has taken place.

For gas generation, as the gas-producing substance,
20   (expanding agent, propellant), sodium azide (NaN_3) has
hitherto chiefly been used as the fuel . The great
advantage of azide generators is that the gas liberated
consists of nitrogen to the extent of almost 100 per
cent and therefore is not a health risk. Because of the
25   high toxicity of sodium azide (LD_{50} value of 27 mg/kg),
which is comparable to that of potassium cyanide
(cyanide of potassium), however, with further use the
problems of disposal and recycling of airbag gas
generators in resulting scrap vehicles and the hazards
30   and risks of criminal misuse would become ever greater.

Possible alternative substances are organic nitrogen-
rich compounds, which achieve good performance values
(gas yield, pressure course etc.) similar to those of

sodium azide. Extensive studies and analyses by the Applicant have shown that 5-aminotetrazole is suitable as an environment-friendly alternative fuel. The result was an expanding agent of 5-aminotetrazole, oxidizing

5   agents and additives, which is called SINCO.

When the alternative solid fuels such as 5-aminotetrazole burn up, in addition to the non-toxic working gases nitrogen, carbon dioxide and water vapour,

10   amounts of the toxic gases carbon monoxide, nitrogen monoxide and nitrogen dioxide are formed.

An object of the present invention has therefore been to achieve minimization of the harmful gas concentrations

15   when the alternative solid fuels are employed.

Formation of NO (all types) is in general favoured at higher temperatures and longer residence times of the gases and waste gases in the high temperature range.

20   The processes known hitherto in the prior art for reducing the amount of nitrogen oxide are chiefly based on lowering the combustion temperature. Additional thermal formation of NO is prevented by rapid cooling of the waste gases. However, the low combustion

25   temperatures have the disadvantage that they increase the formation of CO. Non-uniform combustion processes can lead to marked formation of both harmful gases. Local or brief overheating thus causes the formation of NO, and local or brief undercooling causes the formation

30   of CO.

An alternative for suppressing NO is combustion in catalyst-coated pores or capillary spaces. Catalytic combustion processes are very low in harmful substances,

35   but also sensitive with respect to the operating conditions and require expensive catalyst materials.

Summary Of The Invention

The object underlying the invention has been solved by introduction of substances into the flow path of the working gas, for example by coating components of the gas generator. The substance introduced is vaporized

5   here by the heat of combustion, which, in a homogeneous gas phase reaction, has the effect of converting the harmful gases into non-toxic compounds.

The substances to be employed according to the invention

10 for reducing the amount of nitrogen oxides for use in airbag gas generators must meet the following requirements:

● Non-toxic

15   → Problems during disposal or recycling are thus avoided.

● Melting point > 105°C

→ In strong sunlight, the airbag module can be

20   heated up to 105°C. It must be ensured that the additive does not liquefy and be discharged from the airbag module in such a case. Only substances having a melting point > 105°C are therefore suitable.

25

● Vaporization below 400°C

→ At the places in the gas generator where the additive is to vaporize, temperatures no higher than 400°C are to occur due to the rapid cooling of

30   the gas.

● Long-term stability (15 years)

→ A gas generator should be fully functional over the entire life of a car (up to 15 years).

35

No danger to health from the gases formed

→ The gases liberated during the vaporization
should not be a health hazard and also should

5   undergo no reactions which lead to toxic compounds.

• Effect of reducing the amount of nitrogen oxides

→ The substance introduced should have the effect
of reducing the nitrogen oxides in a homogeneous

10   gas phase reaction.

• Inexpensive

These criteria are met by the following substances,

15   which can be classified into three groups (Table 1).

Metallocenes and their derivatives	Urea and urea derivatives	Sulphur and sulphur compounds
ferrocene 1,1'-diacetylferrocene titanocene pentasulphide	Urea N-formylurea N,N'-dimethylurea N,N-dimethylurea	sulphur (titanocene pentasulphide)

Table 1: Overview of the substances employed

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INSB1

The experiments were carried out in an apparatus which
allows measurement of the variation of concentration
with respect to time of nitrogen monoxide and nitrogen
dioxide in a reaction container of 60 l capacity.

30

The flow diagram of the process in the test apparatus is
shown in figure 1. It can be divided into the following
equipment components:

35   • the gas feed

• the batch reactor

• the nitrogen oxide analyzer with its auxiliary

units.

The test apparatus substantially comprises the batch
reactor of plastics material and the nitrogen oxide

5 analyzer. At the start of each experiment, nitrogen
monoxide, which is partly converted into nitrogen
dioxide with atmospheric oxygen in an equilibrium
reaction, is metered into the reactor. The temperature
in the reactor is 45°C in all the experiments. After

10 about 10 minutes, when the nitrogen dioxide
concentration scarcely changes further, the particular
substance is vaporized in the container. The
concentration courses can be determined by regular
recording of the values for the nitrogen dioxide and

15 nitrogen monoxide concentration, and these allow
conclusions to be drawn regarding the activity of the
particular substance.

Results which allow a comparison of substances in

20 respect of their activity in reducing the amount of
nitrogen oxides can be obtained with this test
apparatus.

The experiments have surprisingly shown:

25

- A reduction in the nitrogen dioxide concentration was
achieved with all the substances tested.

- Ferrocene shows the best action. A rapid degradation

30 of nitrogen dioxide is achieved with comparatively
small amounts.

The following experiments are intended to explain the
invention without limiting it:

35

Experimental set-up:

Plastics material was chosen as the material for the reactor in order to avoid reactions which may occur on a

5 metallic wall. The plastics container employed is not very heat-stable. The temperature in the container should therefore not exceed 45°C, so that no deformations of the container wall result. The reactor contains a vaporizer and a fan heater. The vaporizer

10 essentially comprises a heating plate which is continuously temperature-controllable up to 350°C and on which the test substances can be heated to the sublimation or boiling point in a glass dish. The fan heater serves to establish a desired temperature and to

15 thoroughly mix the reaction mixture intensively. Mixing is necessary in order to ensure the same reactant concentrations and temperatures in the entire reactor. The temperature in the reactor can be established and re-adjusted manually with an adjuster connected to the

20 heating of the fan heater. Regulation of the temperature in the container is necessary because of the heat losses via the wall, the heat supplied via the heating plate and the endo- or exothermic reactions which proceed in the reactor. The temperature is

25 measured with a thermocouple connected to a voltmeter.

To measure the concentration of nitrogen oxides (NO, NO_2), a chemiluminescence apparatus is employed, to which the bypass pump, the silica gel drying cartridge

30 and the ozone destroyer/pump unit are also connected. To protect the chemiluminescence apparatus from contamination, a microfibre filter is incorporated between the reactor and the chemiluminescence apparatus.

35 The nitrogen monoxide is fed in with the aid of a gas bag which, filled beforehand, is connected to the three-way stopcock. The calibrating gas (nitrogen with

80 ppm nitrogen monoxide) is passed directly to the chemiluminescence apparatus from the pressure bottle via a pressure reducer. The gas should flow into the analyzer without pressure. Approx. 50% or 0.6 l/min of

5 the amount of gas required must therefore flow out via a T-piece with an excess line. The excess is passed into a fume cupboard. The excess line has a length of more than 2 m, in order to avoid mixing of the calibrating gas with the air of the atmosphere. A flow meter is

10 also installed on the line, so that the predetermined value for the volume flow can be monitored. Only pipes with a smooth surface and made of inert material, such as PTFE, glass or steel, have been used as the gas lines.

15

Experimental procedure:

A specific amount of the substance to be tested is weighed into a glass dish and spread uniformly on the

20 glass base. The glass is then placed in the middle of the heating plate and the temperature setting of the vaporizer is checked. Thereafter, the lid is placed on the plastics container and the lever on the clamping ring is pressed closed. The screw fittings on the

25 container connections are now tightened firmly, so that tightness of the container is ensured. The thermocouple is connected to the voltmeter and the lines from the fume cupboard and filter must be connected to the three-way stopcocks of the container lid, which must be set

30 such that the container is closed off. Calibration can take place while the container air is being heated up to 45°C with the fan heater. As soon as the temperature in the reactor has reached 45°C, nitrogen monoxide is metered into the container via a gas bag at three-way

35 stopcock I, this being partly converted into nitrogen dioxide with atmospheric oxygen by an equilibrium

reaction. As soon as there is nitrogen monoxide in the reactor, measurement of the time is started.

The first measurement value is recorded after about 30
5   seconds and the second after approximately 5 minutes.
With the preheating time, which has been determined
before the measurement, a time at which the vaporizer is
switched on is specified, so that the substance starts
to vaporize after approx. 10 minutes. At this time, a
10   state in which the nitrogen dioxide concentration
changes only slowly has become established in the
plastics container.

Shortly before vaporization of the substance, a
15   measurement value is also read off on the chemi-
luminescence apparatus and entered into the measurement
record. The time intervals between the measurement
points after the boiling point has been reached depend
on the particular course of the reaction resulting with
20   a certain substance. The measurement values are
recorded over a period of 25 - 30 minutes. The
temperature in the reactor must be monitored
continuously throughout the entire measurement, and, if
necessary, re-adjusted manually via an adjuster.
25
When the measurement has ended, the plastics container
must be opened to the ambient atmosphere and must be
vented for at least 15 minutes. The tubes, filter,
container and three-way stopcocks are then cleaned
30   thoroughly and dried.

Experimental programme:

Three experiments were first carried out without
35   vaporization of an additive. The variation of
concentration of nitrogen monoxide and nitrogen dioxide
without the influence of a substance converted into the

gas phase could be plotted as a result. Comparison of the values determined experimentally with those calculated theoretically was furthermore possible.

5   Table 2 shows a summary of the experiments carried out with the additives.

Table 2. Summary of the experiments carried out

Ferrocene			
Amount of substance [g]	0.015	0.0225	0.03
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture	-	3	-
1,1'-Diacetylferrocene			
Amount of substance [g]	0.05	0.1	-
Number of measurements with NO/NO_2 gas mixture	3	3	-
Titanocene pentasulphide			
Amount of substance [g]	0.05	0.1	0.15
Number of measurements with NO/NO_2 gas mixture	3	3	3
Urea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
N-formylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
N,N'-Dimethylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture	-	3	-
N,N-Dimethylurea			
Amount of substance [g]	0.1	0.4	0.7
Number of measurements with NO/NO_2 gas mixture	3	3	3
Sulphur			
Amount of substance [g]	0.05	0.1	0.15
Number of measurements with NO/NO_2 gas mixture	3	3	3
Number of measurements with $NO/NO_2/CO$ gas mixture		3	

It can be seen from Table 2 that with some substances -
one substance was chosen from each substance group - the

influence of carbon monoxide gas on the reactions proceeding in the container was additionally also investigated.

Influence of ferrocene on the nitrogen oxide concentrations:

The effects on the nitrogen monoxide and nitrogen dioxide concentrations which result due to vaporization of 0.015 g ferrocene were determined in the test apparatus. In the initial phase of the measurement, the variation of the concentrations with respect to time is as expected. The nitrogen monoxide concentration falls due to oxidation of the nitrogen monoxide with atmospheric oxygen, as a result of which the nitrogen dioxide concentration increases. As soon as the ferrocene is in the gas phase (after 540 s), a steep, virtually linear drop in the nitrogen dioxide concentration starts. It decreases by 40 ppm within 35 seconds. During this period of time, the nitrogen monoxide concentration remains constant at a value of 178 ppm. It then falls further, and the nitrogen dioxide concentration increases again.

To check the 1st measurement, two further experiments were carried with 0.015 g ferrocene and similar nitrogen oxide concentrations. The same variation in concentration as in the 1st measurement is found in each of the two repeat measurements. As soon as the ferrocene is in the gas phase, a rapid drop in the nitrogen dioxide concentrations takes place. In experiment no. 2 this is 39 ppm in 43 s, and in experiment no. 3 it is 45 ppm in 45 s. The nitrogen monoxide concentrations remain at a constant value during this period.

If the amount of ferrocene is increased to 0.0225 g, the drop in the concentration of the nitrogen dioxide gets

bigger. The concentration falls by 90 ppm in 88 s.
This approximately corresponds to twice as great a
reduction as in the experiments with an amount of
0.015 g ferrocene.

On the other hand, a further increase in the amount of
substance to 0.03 g brings no further increase in the
lowering of the concentration. The nitrogen dioxide
concentration is lowered by 88 ppm within 75 s. The
results were in each case confirmed in two further
measurements.

The values for the decrease in nitrogen dioxide for all
the measurements are summarized in Table 3.

Table 3: <u>Summary of the lowering of nitrogen dioxide by
ferrocene in the gas phase</u>

	0.015 g ferrocene	0.0225 g ferrocene	0.3 g ferrocene
Experiment no. 1	40 ppm	90 ppm	88 ppm
Experiment no. 2	39 ppm	70 ppm	80 ppm
Experiment no. 3	45 ppm	82 ppm	83 ppm

The combustion gases of a gas generator also contain
amounts of carbon monoxide, in addition to the nitrogen
oxides. Three measurements were therefore carried out
additionally with carbon monoxide gas, with an amount of
0.03 g ferrocene and the same experimental conditions as
in the previous experiments, in order to detect possible
influences of carbon monoxide on the results. The ratio
of CO to NO_2 in the combustion gases of the gas
generator is about 10 to 1. This concentration ratio
was established in the reactor. The CO gas content was
measured with Dräger tubes (relative standard deviation:
± 10 to 15%). The results show that the variation in
the nitrogen monoxide and nitrogen dioxide
concentrations does not change with carbon monoxide gas.

The values for the reduction in nitrogen dioxide with and without carbon monoxide are compared in Table 4.

**Table 4:** Summary of the decrease in nitrogen dioxide without and without carbon monoxide

	0.03 g ferrocene (without CO)	0.03 g ferrocene (with CO)
Experiment no. 1	88 ppm	91 ppm
Experiment no. 2	80 ppm	85 ppm
Experiment no. 3	83 ppm	86 ppm

Interpretation of the results:

To be able to explain the results of the experiments with ferrocene, an FT-IR analysis of the residue which forms in the reactor was carried out. For this, the reactor was rinsed out with water after an experiment. The resulting mixture was then evaporated in a rotary evaporator. After the residue which remained had been dried in a drying cabinet, the KBr pellet was prepared for the FT-IR analysis and the analysis was then carried out in an FT-IR apparatus.

In addition to the FT-IR analysis, a GC analysis was also carried out for identification of the gaseous products. For this, 100 mg ferrocene were kept in a headspace glass at 80°C for 2 hours in order to convert some of the ferrocene into the gas phase. Thereafter, 3 ml of an NO/NO_2 mixture were added to the glass. 2 ml of gas from the headspace glass were analyzed in a gas chromatograph. It was found that, in addition to the ferrocene and air constituents, the gas phase also additionally contained cyclopentadiene.

It can be concluded from the above investigations that ferrocene reacts with nitrogen dioxide in a redox reaction to give iron(III) oxide, cyclopentadiene and nitrogen.

$$4 \; Fe \quad + \quad 3 \, NO_2 \quad \longrightarrow \quad 2 \, Fe_2O_3 \quad + \quad 8 \bigcirc \quad + \quad 1,5 \, N$$

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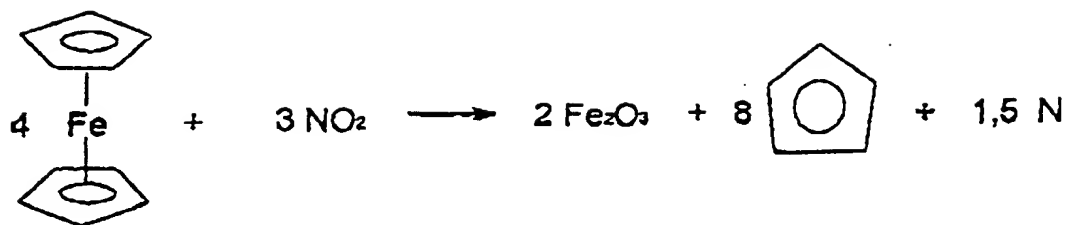
The rapid decrease in the nitrogen dioxide
concentrations in the experiments can be explained by

10   this equation. The constant nitrogen monoxide values
could be attributed to the fact that the nitrogen
dioxide is only partly reduced to nitrogen monoxide and
the formation and degradation are therefore in
equilibrium.

15

**Influence of 1,1'-diacetylferrocene on the nitrogen
oxide concentrations:**

The variation in nitrogen oxide concentration in an

20   experiment with 0.1 g 1,1'-diacetylferrocene was
investigated. Until this substance vaporizes, the
concentrations change as expected. The nitrogen
monoxide values fall due to oxidation and the nitrogen
dioxide values increase. Shortly after the start of the

25   vaporization operation, the nitrogen monoxide
concentration increases by 24 ppm in 233 s - initially
sharply, then becoming less intense. The nitrogen
dioxide concentration similarly falls by 26 ppm. The
normal NO/NO_2 equilibrium course is then established

30   again.

The results of the 1st experiment were confirmed in two
further measurements with 0.1 g 1,1'-diacetylferrocene.
In the 2nd experiment, a decrease in the NO_2

35   concentration by 23 ppm and an increase in the NO
concentration by 25 ppm occurred in 262 s. In a 3rd

experiment, it was found that the NO_2 values fall by
24 ppm and the NO values rise by 23 ppm in 250 s.

When only 0.05 g 1,1'-diacetylferrocene was introduced
5   into the gas phase, it was found that the values for the
decrease in nitrogen dioxide and for the increase in
nitrogen monoxide were lower by about half compared with
the experiments with 0.1 g (Table 5). Qualitatively,
however, the courses of the concentrations as a function
10   of time are identical.

All the results of the experiments with 1,1'-
diacetylferrocene are summarized in Table 5.

15   **Table 5**: <u>Summary of the increase and decrease
respectively in the concentrations of NO and NO_2</u>

	0.05 g 1,1'-diacetylferrocene		0.1 g 1,1'-diacetylferrocene	
	NO	NO_2	NO	NO_2
Experiment no. 1	+13 ppm	-13 ppm	+24 ppm	-26 ppm
Experiment no. 2	+12 ppm	-11 ppm	+25 ppm	-23 ppm
Experiment no. 3	+11 ppm	-11 ppm	+23 ppm	-24 ppm

Interpretation of the results:
25   It can be seen from Table 5 that a decrease in nitrogen
dioxide results in a corresponding increase in nitrogen
monoxide. This effect is probably due to a redox
reaction of the 1,1'-diacetylferrocene with the nitrogen
dioxide, which is accordingly reduced to nitrogen
30   monoxide. Compared with ferrocene, the ferrocene
derivative 1,1'-diacetylferrocene is a much poorer
reducing agent with the additional disadvantage of the
formation of nitrogen monoxide.
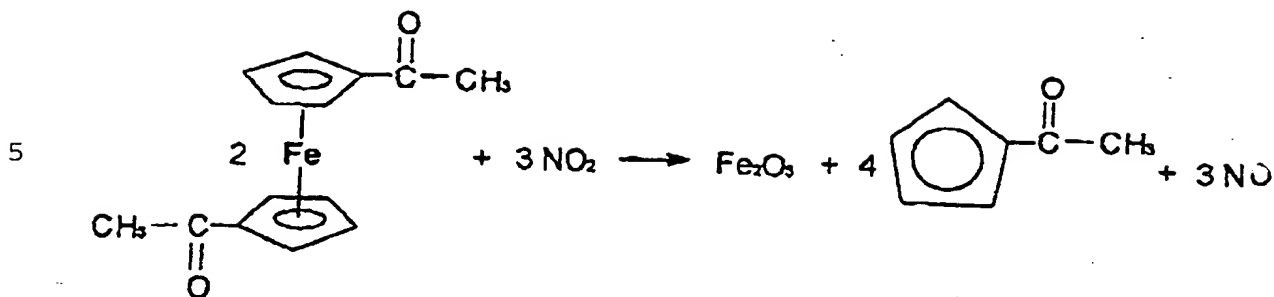
Influence of titanocene pentasulphide on the nitrogen
oxide concentrations:

The effects on nitrogen monoxide and nitrogen dioxide
which result from vaporization of 0.05 g titanocene
pentasulphide were investigated. The nitrogen dioxide
concentration falls virtually linearly from 253 ppm to
225 ppm in 85 s due to titanocene pentasulphide in the
gas phase. In contrast, the nitrogen monoxide
concentration increases in the same way from 269 ppm to
298 ppm. Before the vaporization and after the reaction
of the titanocene pentasulphide with the nitrogen
oxides, the normal variations concentration courses
occur, i.e. decrease in the nitrogen monoxide due to
oxidation and, as a consequence, an increase in the
nitrogen dioxide.

Two further experiments with 0.05 g titanocene
pentasulphide led to results similar to those in the 1st
experiment. The precise values for the changes in the
concentrations can be seen from Table 6, in which all
the results of the three measurements are summarized.

Table 6: <u>Summary of the increase and decrease</u>
<u>respectively in the concentrations of NO and NO_2</u>

	0.05 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	77	+29	-28
Experiment no. 2	85	+25	-24
Experiment no. 3	76	+23	-26

By increasing the amount of the substance from 0.05 to
0.1 g, the values for the nitrogen monoxide increase and
the nitrogen dioxide decrease have approximately
doubled. In 103 s, the nitrogen dioxide concentration
fell by 50 ppm from 351 ppm to 301 ppm. In the same
period of time, the nitrogen monoxide concentration rose
by 48 ppm from 306 ppm by 48 ppm to 354 ppm. Two
further experiments with 0.1 g titanocene pentasulphide
give results which are in agreement, these being
summarized in Table 7.

Table 7: <u>Overview of the increase and decrease</u>
<u>respectively in the concentrations of NO and NO_2</u>

	0.1 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	103	+48	-50
Experiment no. 2	108	+51	-53
Experiment no. 3	100	+55	-56

An increase in the amount of the substance to 0.15 g had
the effect of a further decrease in the nitrogen dioxide
and a corresponding increase in the nitrogen monoxide.
The nitrogen monoxide concentration rises by 75 ppm in
130 s, and at the same time the nitrogen dioxide

concentration falls by 77 ppm. Comparable results are achieved in the two repeat experiments, which are shown in figures A.19 and A.20 in the appendix (see Table 8).

5 Table 8: <u>Summary of the increase and decrease respectively in the concentrations of NO and NO$_2$</u>

	0.15 g titanocene pentasulphide		
	Period [s]	NO [ppm]	NO$_2$ [ppm]
Experiment no. 1	130	+75	-77
Experiment no. 2	115	+70	-68
Experiment no. 3	125	+68	-72

Interpretation of the results:

15 An FT-IR analysis of the residue which has formed in the reactor should provide information on the reaction mechanism. In the FT-IR spectrum obtained, everything indicates that the residue comprises titanocene pentasulphide and titanium(IV) oxide (TiO$_2$). There is

20 accordingly very probably a redox reaction of the titanocene pentasulphide with nitrogen dioxide, in which the reaction products cyclopentadiene, nitrogen monoxide, titanium(IV) oxide and sulphur are formed. This explains the simultaneous formation of nitrogen

25 monoxide during the degradation of nitrogen dioxide.

30
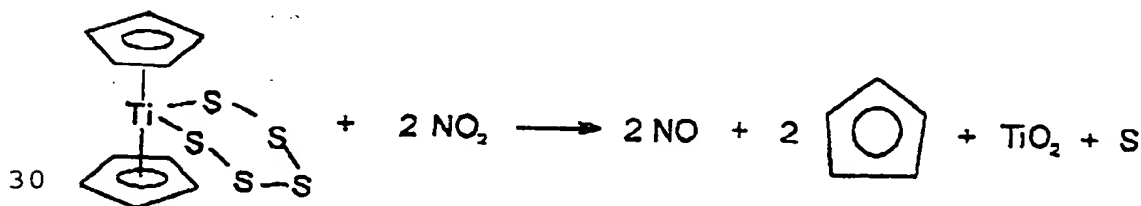
<u>Influence of urea on the nitrogen oxide concentrations:</u>

35 There are no striking changes in the variation in concentration of nitrogen monoxide when urea is

vaporized in the reactor. In contrast, a decrease in the concentration of nitrogen dioxide from 82 ppm to 54 ppm occurs. This reduction by 28 ppm takes place in 410 s. Thereafter, the nitrogen dioxide values increase

5   again slowly. The two repeat experiments confirm these results. All the results of the experiments with 0.1 g urea are shown in Table 9.

Table 9: Summary of the decrease in the NO$_2$
10   concentration

	0.1 g urea	
	Period [s]	NO$_2$ [ppm]
Experiment no. 1	410	-28
Experiment no. 2	420	-26
Experiment no. 3	470	-32

If 0.4 g urea is employed, the nitrogen dioxide is degraded to a significantly greater extent compared with
20   the addition of 0.1 g urea. In the first 300 s after the start of the vaporization process, a relatively rapid decrease in the nitrogen dioxide concentration takes place. The values then fall further at a decreasing rate. At the end of the measurement, a
25   lowering of the nitrogen dioxide concentration is still detectable. Overall, a reduction in the nitrogen dioxide by 111 ppm takes place in 20 min. All the results which were achieved with 0.4 g urea are shown in Table 10.

30

Table 10: <u>Summary of the decrease in the NO_2</u>
<u>concentration</u>

	0.4 g urea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	1200	-111
Experiment no. 2	1200	-108
Experiment no. 3	1200	-114

An increase in the amount of urea to 0.7 g leads to even
higher values for the decrease in nitrogen dioxide. A
reduction in the nitrogen dioxide concentration by
179 ppm in 1,200 s is found. The qualitative variation
of the measurement values is otherwise identical to the
variation which resulted when 0.4 g urea was employed.
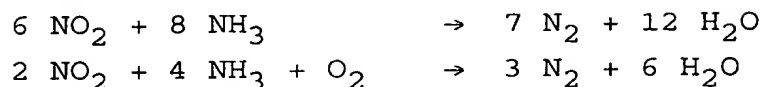The results of the repeat experiments can be seen from
Table 11.

Table 11: <u>Summary of the decrease in the NO_2</u>
<u>concentration</u>

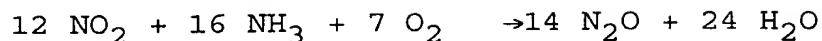|	0.7 g urea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	1200	-179
Experiment no. 2	1200	-200
Experiment no. 3	1200	-188

Interpretation of the results:
When urea is heated above its melting point, ammonia
(NH_3), which is known as a reducing agent for nitrogen
oxide reduction, is formed. It is to be assumed that
the degradation of nitrogen dioxide takes place by a
homogeneous gas phase reaction of ammonia with nitrogen
dioxide. The reduction of the NO_2 with NH_3 can be
described by the following overall reaction equations:

Main reactions

$$6 \ NO_2 + 8 \ NH_3 \qquad \rightarrow \quad 7 \ N_2 + 12 \ H_2O$$
$$2 \ NO_2 + 4 \ NH_3 + O_2 \quad \rightarrow \quad 3 \ N_2 + 6 \ H_2O$$

5   **Side reaction**

$$12 \ NO_2 + 16 \ NH_3 + 7 \ O_2 \quad \rightarrow 14 \ N_2O + 24 \ H_2O$$

- Nitrogen (N_2) and water vapour are formed in the main
  reactions as reaction products of this selective
10   reduction. The undesirable dinitrogen monoxide (N_2O)
  from the side reaction does not appear to be formed to
  a substantial extent.

Nitrogen monoxide is slow to react compared with
15   nitrogen dioxide. This could be the reason why the
nitrogen monoxide is not reduced with ammonia at a
temperature of 45°C.

Influence of N-formylurea on the nitrogen oxide
20   **concentrations:**

On vaporization of 0.1 g N-formylurea, the nitrogen
dioxide concentration starts to fall relatively slowly
from the time 750 s to the time 1,230 s. The
25   concentration is reduced from 162 ppm by 12 ppm to
150 ppm during this period. Thereafter, the values
remain approximately constant. No striking changes are
detectable in the course of the nitrogen monoxide
concentration.
30

All the results achieved in the 3 experiments with 0.1 g
N-formylurea are summarized in Table 12.

Table 12: Summary of the decrease in the NO_2 concentration

	0.1 g N-formylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	480	-12
Experiment no. 2	500	-14
Experiment no. 3	450	-14

To investigate the effects on the nitrogen oxides when the amount of the substance is increased, in each case 3 experiments were carried with 0.4 g and 0.7 g N-formylurea.

The nitrogen dioxide concentration falls by 63 ppm in 460 s by vaporization of 0.4 g N-formylurea. Similar results are achieved in the 2nd and 3rd experiment with an NO_2 reduction of 54 ppm and 66 ppm respectively. Table 13 gives a summary of all the results. There are no changes in the qualitative variation in the concentrations compared with the experiments with 0.1 g.

Table 13: Summary of the decrease in the NO_2 concentration

	0.4 g N-formylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	460	-63
Experiment no. 2	480	-54
Experiment no. 3	480	-66

In contrast to the experiments with an amount of the substance of 0.1 g and 0.4 g, the nitrogen dioxide concentration still continues to fall slowly, after a relatively rapid decrease, when 0.7 g N-formylurea is employed. In a chosen period of 1,000 s, a reduction in

nitrogen dioxide by 85 ppm thus results.   Two repeat
experiments confirm this result (see Table 14)

Table 14: <u>Summary of the decrease in the NO$_2$ concentration</u>

	0.7 N-formylurea	
	Period [s]	NO$_2$ [ppm]
Experiment no. 1	1000	-85
Experiment no. 2	1000	-94
Experiment no. 3	1000	-80

Interpretation of the results:

When N-formylurea is heated above its melting point,
ammonia is probably formed.   The homogeneous gas phase
reactions which take place as a result are the same as
those described for urea.   N-Formylurea has a higher
molecular weight than urea because of the formyl group.
As a result, less ammonia is formed with N-formylurea
than with urea when the same amounts are vaporized.
This explains the poorer values for the reduction of
nitrogen dioxide compared with the experiments with
urea.

**Influence of N,N'-dimethylurea on the nitrogen oxide
concentrations:**

The influence of 0.1 g N,N'-dimethylurea was
investigated.   No changes were found in nitrogen
monoxide compared with the normal concentration course.
In contrast, the content of nitrogen dioxide is
decreased by 48 ppm in 465 s.   After this decrease, the
values for the nitrogen dioxide concentration remain
virtually constant to the end of the measurement.   The
results of all three experiments with 0.1 g N,N'-
dimethylurea are shown in Table 15.   The results of the
repeat experiments show no substantial differences from

the first experiment here.

Table 15: Summary of the decrease in the NO$_2$
concentration

	0.1 g N,N'-dimethylurea	
	Period [s]	NO$_2$ [ppm]
Experiment no. 1	465	-48
Experiment no. 2	497	-40
Experiment no. 3	506	-38

The vaporization of 0.4 g N,N'-dimethylurea in the
reactor leads to the following changes in the variation
in the NO$_2$ concentration. The nitrogen dioxide
concentration falls from 210 ppm by 106 ppm to 102 ppm
in 286 s. Thereafter, the measurement values increase
again comparatively slowly. In the 2nd and 3rd
experiments with 0.4 g N,N'-dimethylurea, values of
101 ppm and 102 ppm respectively result for the
decrease in nitrogen dioxide. All the results are again
summarised in Table 16.

Table 16: Summary of the decrease in the NO$_2$
concentration

	0.4 g N,N'-dimethylurea	
	Period [s]	NO$_2$ [ppm]
Experiment no. 1	286	-106
Experiment no. 2	320	-101
Experiment no. 3	334	-102

Increasing the amount of the substance to 0.7 g produced
no significant increase in the values for the decrease
in nitrogen dioxide compared with the experiments with
0.4 g. It was found that the nitrogen dioxide
concentration decreases by 105 ppm over a period of

675 s. The results of the two repeat experiments, in addition to this result, are also shown in Table 17.

Table 17: <u>Summary of the decrease in the NO_2 concentration</u>

	0.7 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	675	-105
Experiment no. 2	725	-108
Experiment no. 3	716	-111

To be able also to investigate possible influences of carbon monoxide, three experiments were carried out with 0.1 g N,N'-dimethylurea and a carbon monoxide/nitrogen oxide mixture. Compared with the measurement without carbon monoxide, as in the two repeat experiments, there are no striking changes. Table 18 summarizes the results with and without carbon monoxide.

Table 18: <u>Summary of the decrease in nitrogen dioxide without and with carbon monoxide</u>

	0.1 g N,N'-dimethylurea (without CO)		0.1 g N,N'-dimethylurea (with CO)	
	Period [s]	NO_2 [ppm]	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48	492	-39
Experiment no. 2	497	-40	550	-46
Experiment no. 3	506	-38	532	-40

Interpretation of the results:

When N,N'-dimethylurea is heated above the melting point, ammonia probably forms and reduces some of the nitrogen dioxide by homogeneous gas phase reactions. If the results are compared with those which were achieved in the experiments with urea, it becomes clear that the

action is poorer if N,N'-dimethylurea is used, apart from the experiments with an amount of the substance of

0.1 g. As with N-formylurea, the poorer values for the nitrogen dioxide degradation are related to the

5 higher molecular weight and the smaller amount of ammonia thus formed on heating. The better values compared with the experiments with an amount of substance of 0.1 g possibly result from a positive influence of the two methyl groups. This may also be

10 the reason why the values for the nitrogen dioxide degradation are greater compared with those of the experiments with N-formylurea.

Influence of N,N'-dimethylurea on the nitrogen oxide
15 concentrations:

The influence on the nitrogen oxide concentrations by vaporization of 0.1 g N,N'-dimethylurea was investigated. No changes were found in nitrogen

20 monoxide compared with the normal concentration course. In contrast, the content of nitrogen dioxide is decreased by 48 ppm in 465 s. After this decrease, the values for the nitrogen dioxide concentration remain virtually constant to the end of the measurement. All

25 the results of the three experiments with 0.1 g N,N'-dimethylurea are shown in Table 19. The results of the repeat experiments show no substantial differences from the first experiment here.

30 **Table 19:** Summary of the decrease in the NO_2 concentration

	0.1 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	465	-48
Experiment no. 2	497	-40
Experiment no. 3	506	-38

The vaporization of 0.4 g N,N'-dimethylurea in the
reactor leads to changes in the variation in NO_2
concentration.   The nitrogen dioxide concentration falls
from 210 ppm by 106 ppm to 102 ppm in 286 s.
Thereafter, the measurement values increase again
comparatively slowly.   In the 2nd and 3rd experiments
with 0.4 g N,N'-dimethylurea, values of 101 ppm and 102
ppm respectively are obtained for the decrease in
nitrogen dioxide.   All the results are again summarized
in Table 20.

Table 20: <u>Summary of the decrease in the NO_2</u>
<u>concentration</u>

	0.4 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	286	-106
Experiment no. 2	320	-101
Experiment no. 3	334	-102

Increasing the amount of the substance to 0.7 g produced no significant increase in the values for the decrease in nitrogen dioxide compared with the experiments with 0.4 g. The nitrogen dioxide concentration decreases by 105 ppm over a period of 675 s. The results of the two repeat experiments, in addition to this result, are also shown in Table 21.

Table 21: <u>Summary of the decrease in the NO_2</u>
<u>concentration</u>

	0.7 g N,N'-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	675	-105
Experiment no. 2	725	-108
Experiment no. 3	716	-111

To be able also to investigate possible influences of carbon monoxide, three experiments were carried out with 0.1 g N,N'-dimethylurea and a carbon monoxide/nitrogen oxide mixture. Compared with the measurement without carbon monoxide, as in the two repeat experiments, there are no striking changes. Table 22 summarizes the results with and without carbon monoxide.

Table 22: Summary of the decrease in nitrogen dioxide without and with carbon monoxide

	0.1 g N,N'-dimethylurea (without CO)		0.1 g N,N'-dimethylurea (with CO)	
	Period [s]	NO$_2$ [ppm]	Period [s]	NO$_2$ [ppm]
Experiment no. 1	465	-48	492	-39
Experiment no. 2	497	-40	550	-46
Experiment no. 3	506	-38	532	-40

Interpretation of the results:

When N,N'-dimethylurea is heated above its melting point, ammonia probably forms and reduces some of the nitrogen dioxide by homogeneous gas phase reactions. If the results are compared with those which were achieved in the experiments with urea, it becomes clear that the action is poorer if N,N'-dimethylurea is used, apart from the experiments with an amount of the substance of 0.1 g. As with N-formylurea, the poorer values for the nitrogen dioxide degradation are related to the higher molecular weight and the smaller amount of ammonia thus formed on heating. The better values compared with the experiments with an amount of substance of 0.1 g possibly result from a positive influence of the two methyl groups. This may also be the reason why the values for the nitrogen dioxide degradation are higher compared with those of the experiments with N-formylurea.

Influence of N,N-dimethylurea on the nitrogen oxide concentrations

A reduction in the nitrogen dioxide concentration by 46 ppm was achieved by vaporization of 0.1 g N,N-dimethylurea. It decreases from 102 ppm to 66 ppm in 690 s, and then rises again slightly. N,N-Dimethylurea

evidently has no influence on the nitrogen monoxide.
Experiments nos. 2 and 3 give results which are in
agreement. All the results of the three experiments are
summarized in table 23.

5

Table 23: Summary of the decrease in the NO_2 concentration

	0.1 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	690	-46
Experiment no. 2	650	-40
Experiment no. 3	690	-42

15   0.4 g N,N-dimethylurea had the effect of doubling the
values for the decrease in nitrogen dioxide in a shorter
period of time compared with the experiments with 0.1 g.
The results of the three experiments carried out are
summarized in Table 24.

20

Table 24: Summary of the decrease in the NO_2 concentration

	0.4 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	285	-87
Experiment no. 2	285	-91
Experiment no. 3	285	-96

30   A further decrease in the NO_2 concentration could be
achieved with 0.7 g N,N-dimethylurea. The NO_2 content
decreases by 101 ppm in 330 s. The corresponding values
of the two repeat experiments are shown in Table 25.

Table 25: Summary of the decrease in nitrogen dioxide

	0.7 g N,N-dimethylurea	
	Period [s]	NO_2 [ppm]
Experiment no. 1	330	-101
Experiment no. 2	320	-105
Experiment no. 3	300	-104

Interpretation of the results:

The results of the experiments with N,N'-dimethylurea
and N,N-dimethylurea are very similar. Consequently,
the different arrangement of the methyl groups on the
urea does not have such great importance. The
explanation of the results is analogous to that for the
experiments with N,N'-dimethylurea.

**Influence of sulphur on the nitrogen oxide
concentrations:**

By employing 0.05 g sulphur, a decrease in the nitrogen
dioxide concentration by 20 ppm and an increase in the
nitrogen monoxide concentration by 9 ppm take place
within 355 s. Thereafter, the nitrogen dioxide
increases again slowly due to oxidation of the nitrogen
monoxide, which decreases as a result. The two repeat
experiments lead to results which are in agreement, as
shown in Table 26.

Table 26: Summary of the increase and decrease
respectively in the concentrations of NO and NO_2

	0.05 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	355	+9	-20
Experiment no. 2	360	+10	-19
Experiment no. 3	345	+8	-22

In an experiment with 0.1 g sulphur, slightly different values for the NO increase and the NO_2 decrease result compared with the experiment with 0.05 g sulphur. Over a period of 375 s, the nitrogen dioxide concentration decreases by 30 ppm and the nitrogen monoxide concentration increases by 10 ppm. These values are confirmed by Experiments nos. 2 and 3. The results of all the measurements with 0.1 g sulphur are shown in Table 27.

Table 27: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

	0.1 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	375	+10	-30
Experiment no. 2	360	+10	-30
Experiment no. 3	360	+11	-32

The nitrogen dioxide concentration could be lowered still further with an amount of sulphur of 0.15 g, but the nitrogen monoxide concentration also rose somewhat. The nitrogen dioxide content decreases by 39 ppm within 370 s, while the nitrogen monoxide content increases by 21 ppm. The two repeat experiments produce corresponding results, which are also shown in Table 28.

Table 28: Summary of the increase and decrease respectively in the concentrations of NO and NO_2

|	0.15 g sulphur		
	Period [s]	NO [ppm]	NO_2 [ppm]
Experiment no. 1	370	+21	-39
Experiment no. 2	420	+28	-40
Experiment no. 3	410	+22	-41

Three experiments were additionally also carried out with 0.1 g sulphur and a carbon monoxide/nitrogen oxide mixture. As can be seen from Table 29, no effect of the carbon monoxide on the results can be detected. The nitrogen dioxide concentration decreases by 31 ppm in 390 s and the nitrogen monoxide concentration increases by 10 ppm.

Table 29: <u>Increase and decrease respectively in the concentrations of NO and NO$_2$ with and without CO</u>

	0.1 g sulphur (without CO)			0.1 g sulphur (with CO)		
	Period [s]	NO [ppm]	NO$_2$ [ppm]	Period [s]	NO [ppm]	NO$_2$ [ppm]
Experiment no. 1	375	+10	-30	390	+8	-31
Experiment no. 2	360	+10	-30	425	+10	-32
Experiment no. 3	360	+11	-32	410	+14	-33

Interpretation of the results:

Sulphur self-ignites at approx. 260°C and burns with a weak blue flame to give sulphur dioxide and up to 40% sulphur trioxide. Below 300°C, NO$_2$ reacts directly with SO$_2$:

$$NO_2 + SO_2 \rightarrow NO + SO_3$$
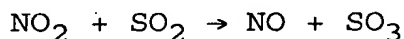
In addition to sulphur trioxide, nitrogen monoxide is also formed in this reaction, and can probably also react with sulphur dioxide:

$$2\ NO + SO_2 \rightarrow N_2O + SO_3$$
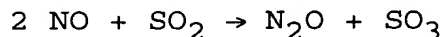
This equation would also explain why NO does not increase at the rate at which NO$_2$ is degraded.